

Analytical use of polyurethane foam sorbents for enrichment processes

I. Enrichment and determination of trace elements in natural waters

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Sorption properties of the polyurethane foam treated by diethylammonium diethyldithiocarbamate have been utilized for enrichment and subsequent determination of Ag, Bi, Cd, Co, Cu, Mn, Ni, Pb, Sb, Sn, V, and Zn in drinking and river waters. Matrix elements as Al, Ca, Fe, Mg, and Si are not sorbed under the given conditions, the sorption of metal and transition elements is accomplished with a high separation yield and 1 : 100 or higher enrichment ratio. For final determination, the energy dispersive XRF spectrometry, AAS with flame atomization or AES-ICP method were applied.

Both control and monitoring of the water pollution require complex approach. Multicomponent quantitative determination of trace elements is an important part of the water analysis. Usually, the concentration of trace elements in natural water is in the range $\langle 0.01, 10 \rangle \mu\text{g dm}^{-3}$. The limit of detection of the spectroscopic methods, however, not always and not for each element corresponds to this criterion. Therefore, chemical operations are involved prior to the determination of these elements.

Environmental, as well as drinking waters contain, except trace elements, also major elements, *i.e.* matrix components (alkali metals and alkali earth metals), which usually have to be separated before the determination of trace elements in order to increase their limits of detection and the selectivity of the determination. Therefore, it is necessary to use such procedures and reagents, the chemisorption properties of which ensure not only enrichment of the analytically important trace elements, but also the separation of undesirable matrix elements. Solvent extraction, using chelate-forming reagents is a frequently

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applied method for this purpose. The degree of enrichment in this method is limited, among others, by the solubility of organic solvents in water. One of the ways to eliminate this shortcoming is the use of foamed sorbents [1—4]. Solid polyurethane foams have suitable mechanical and chemical properties, moreover, they are cheap and widely available. In preconcentration and/or separation processes it is appropriate to impregnate them with suitable chemisorption or complex-forming agents.

In this work, for the separation and preconcentration of the selected trace elements in the samples of surface and drinking waters a choice of a suitable impregnating agent and conditions of a preconcentration-separation procedure was made using resilient polyurethane foam sorbent.

Experimental

For the separation and preconcentration of trace elements as Ag(I), Bi(III), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II), Sb(III), Sn(II), V(V), and Zn(II) from aqueous samples, an open-cell type polyether-based resilient polyurethane foam (Molitan, Gumotex, Valašské Klobouky, CSFR) was used, impregnated with diethylammonium diethyldithiocarbamate (DDDC).

Before use, the foam was cut by means of a hollow drill in the form of cylinders of $2r = 3.5$ cm, $h = 10$ cm and $2r = 5$ cm, $h = 10$ cm, respectively. The mass of one cylinder was about 2.6 g and 5 g, respectively. It was necessary to remove all impurities from the foam, according to *Braun* and *Palágyi* [4, 5]. The final procedure was as follows. The foam was washed thoroughly three times with diluted HCl ($c = 2$ mol dm⁻³), then with distilled water until neutral reaction, and finally, three times with acetone and then it was dried at 70—80°C. The cleaned and dried foam cylinders were soaked in 1% solution of DDDC in chloroform. The cylinders were squeezed for about 15—30 min to soak them thoroughly with the impregnating reagent. The excess of reagent was removed by squeezing of the foam cylinders between sheets of filtration paper. Finally, the foam cylinders were dried under vacuum at laboratory temperature. After drying, the impregnated cylinders were stored in a refrigerator at 4—6°C and used for the separation not later than after 24 h.

Into a glass column, from the bottom to the top, foam cylinders were placed gradually: one unimpregnated, then one or two impregnated, and an unimpregnated foam disc of about 2—4 cm thickness. Finally, the column filling was compressed to a volume of 35 cm³ or 70 cm³ (the wider column), respectively. After 10 min of evacuation, the column was filled with distilled water [6]. On the top of the column, a sample reservoir was connected. A constant flow rate (20 cm³ min⁻¹) was applied using a peristaltic pump [7].

The sample was represented by a synthetic substitute for the surface water, containing 300 mg dm⁻³ of Ca(II), 200 mg dm⁻³ of Mg(II), and 50 µg dm⁻³ of each of the studied metals. The pH of the sample was adjusted to 1.5 using diluted HNO₃. Prior to the actual

preconcentration, the pH of the sample was adjusted to 4. Besides this, also real tap (drinking) water was examined using three impregnated wider cylinders (Fig. 1).

As the total volume of the sample was pumped through the column (1–5 dm³), the remaining water was sucked out of it, and the column filling was transferred completely into a Soxhlet extraction apparatus, where the metal chelates were reextracted from the foam cylinders by tenfold extraction with chloroform. The organic solvent was distilled off, and the metal chelates of the dithiocarbamate were decomposed by twofold evaporation with concentrated HNO₃ on a sand bath. Finally, after the addition of diluted HNO₃ ($\varphi_r = 1:1, 10\text{ cm}^3$) and a short boiling, the sample was transferred into a 25 or 50 cm³ volumetric flask, thus attaining a preconcentration of the separated trace elements of about two orders of magnitude.

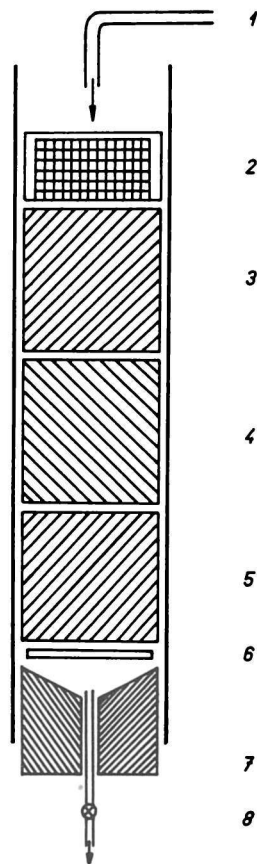


Fig. 1. Schematic representation of the absorption column. 1. Inlet of the sample; 2. unimpregnated polyurethane foam disc; 3, 4. impregnated polyurethane foam cylinders; 5. unimpregnated polyurethane foam cylinder; 6. porous glass insertion or polyurethane foam disc; 7. packing; 8. outlet of the sample.

The actual analytical determination of the separated elements was made by energy dispersive X-ray fluorescence (XRF) spectrometry, or by atomic absorption spectrometry (AAS) in combination with electrothermal atomization, and also by a method of atomic emission spectrometry with inductively coupled plasma (AES-ICP).

Energy dispersive XRF spectrometry

The elements of Z less than 35 and Pb were excited directly with a ^{238}Pu source, the others indirectly with ^{241}Am source through a Dy-target. The energy resolution of the used measuring system equipped with a Si (Li) detector was 200 eV for 5.9 keV energy. The liquid samples were transformed into thin layers [8]. The mineralized samples were transferred into a 400 cm³ beaker. After dilution to 200–250 cm³, addition of 500 µg of Fe(III) and adjusting the pH to 4–4.5 with diluted NH₄OH, 5 cm³ of freshly prepared and filtered solution of ammonium pyrrolidinedithiocarbamate (APDC) was added. After standing for 30 min, the precipitate formed was filtrated off on a Synpor-6 (0.4 µm, $d = 2.5$ cm) membrane filter; the sample diameter on the filter was 2 cm. The drying of the filter was accomplished at laboratory temperature. During the measurement, the filter was fixed between two Mylar films. Calibration samples were prepared in the same way as the samples. The experimentally found limits of detection are listed in Table 1.

Table 1

Experimentally determined limits of detection and guarantee

Element	Limits of			
	detection		guarantee	
	directly $c_L/(\mu\text{g dm}^{-3})$	using IPS $c_L/(\mu\text{g dm}^{-3})$	directly $c_G/(\mu\text{g dm}^{-3})$	using IPS $c_G/(\mu\text{g dm}^{-3})$
Ag	1.5	0.4	3.1	0.8
Bi	1.1	0.3	2.2	0.5
Cd	1.8	0.4	3.5	0.9
Co	1.5	0.4	2.9	0.7
Cu	0.9	0.2	1.7	0.4
Fe	6	1.5	11	2.9
Mn	2.0	0.5	4.0	1.0
Ni	1.4	0.3	2.7	0.7
Pb	1.1	0.3	2.3	0.6
Sb	2.0	0.5	4.0	1.0
Sn	0.9	0.2	1.8	0.4
V	3.3	0.8	6.6	1.7
Zn	1.0	0.2	1.9	0.5

IPS — Impregnated polyurethane sorbents; c_L — determined according to 3 sigma criterion; c_G — determined according to 6 sigma criterion.

Atomic-spectrometric determination

The mineralized extract was made up with distilled water to the mark of a 25 cm³ or 50 cm³ volumetric flask in the case of the drinking water analysis, or of a 100 cm³ and

eventually a 250 cm³ flask in the case of the analysis of medium to highly polluted waste water samples. This extract was then used directly for the analysis. In the quantitative AAS determination the $A(X) = f(c(X))$ calibration function was applied. In the determination with ICP, with regard to the used photographic detection [9], a method of the added reference element was consequently used and the calibration lines were constructed as functions of $\Delta Y(X, R) = f(c(X))$.

Extracts of the drinking waters were analyzed by AAS method with flame atomization with concentrations up to 0.5 mg dm⁻³, or by connection of an AAS 1 N apparatus with a tungsten atomizer, type WETA 82, up to the concentration of 0.5 μg dm⁻³. The excitation of the emission spectra in the ICP source was also verified. The relative precision of the individual methods ranged between 3 % and 10 %, and was markedly element-specific, similarly as their detection power.

Results and discussion

In the selection of the preconcentration-separation method, attention was paid to the foam sorbents based on the open-cell polyurethane impregnated with organic chelating reagents. The use of unimpregnated foams was excluded since it would be necessary to add large amounts of salts or acids to the sample, up to the concentration of several mol dm⁻³, which may cause, among other, considerable sample contamination, or undesired matrix effects in spectral determination.

In the choice of the chelating agent, some requirements have been established as follows:

- preconcentration of several elements at certain pH value;
- separation of trace elements from common matrix elements;
- minimal solubility of the reagent in water at the working pH value;
- availability of the reagents of the required purity.

From the commercially available reagents, the following could be taken into account: diethyldithiocarbamic acid (DDC), dithizone (H₂Dz), 8-hydroxyquinoline (HOx), and 1-(2-pyridylazo)-2-naphthol (PAN). Comparing the literature data it was found that H₂Dz, HOx, and PAN are able to retain considerably fewer elements than DDC [10, 11]. DDC reacts with metals of the first and the second analytical groups giving rise to insoluble chelates in water. Sodium salt of DDC was not suitable, because of its good solubility in water. Diethylammonium salt of DDC fulfilled best the requirements listed above, which made possible to separate up to 15 elements in the range of pH from 4 to 5. Good solubility of this reagent in chloroform enabled to obtain high sorption capacity of the column filling. Thus, 1 g of dry polyurethane foam retained up to 3.7 cm³ of the reagent, *i.e.* 0.19 mmol DDC per 1 g of the foam. The column filling contained 0.48 mmol DDC, which equals to 0.24 mmol

capacity of bivalent cations. The chelates of metals are well soluble in organic solvents. Their mineralization and dissolution in distilled water is possible by evaporation with concentrated HNO_3 .

The choice of the working pH value was influenced, besides the number of extractable elements, by washing out the reagent from the foam. With increasing pH value the dissociation of the reagent also increases and its solubility and washing out with water, too. At values of pH higher than 5, the sample flowing out of the column was beclouded with the outwashed reagent. Compression of the foam filling to the 1/6 of its original (released) volume caused an unfavourable decrease in the flow rate. Before the column filling with water, it was necessary to deprive the column of air by means of an exhaustor. In the case that the air was not removed from the column, the sample did not flow through the whole section of the column and the results became irreproducible.

For the extraction of the metal chelates from the polyurethane foam column four solvents were tested: acetone, chloroform, ethyl and n-amyl acetates. The effect of these solvents on the separation yield of the overall procedure (sorption, reextraction, mineralization) is shown in Table 2. It is evident from these results that both the esters are not effective in the reextraction of the complexes of Ag, Cd, Cu, and Pb. Further preliminary tests with the other transition elements gave identical results. The choice of chloroform as the extraction agent was motivated with the same efficiency as that of acetone, as well as with its higher working safety.

Table 2

Elution yield of the individual elements in tested solvents

Solvent	Boiling point	Yield/%			
	°C	Cu	Pb	Ag	Cd
Acetone	56.3	92.7	92.4	91.8	91.2
Chloroform	61.2	91.0	92.4	91.4	91.4
Ethyl acetate	77.1	83.5	90.8	88.8	88.1
n-Amyl acetate	148.8	84.8	73.0	88.1	82.6

The decrease in the separation yield when esters were used, especially in the case of n-amyl ester, could be caused by a higher boiling point of the solvent. At higher temperature a partial destruction of the polyurethane foam began to take place and the outwashed organic substances could not be decomposed even using fivefold evaporation with concentrated HNO_3 . The residues of the organic substances interfered in further determination. When using acetone the reex-

traction proceeded continually; 30 min was chosen. Finally, the chelates were extracted with chloroform in a Soxhlet extractor by tenfold repeated operation. The extraction yields are listed in Table 3.

Table 3

Overall separation yield of the preconcentration-separation procedure using impregnated polyurethane foam sorbents

Element	Yield/%	Element	Yield/%
Ag	91.4	Ni	85.2
Bi	92.0	Pb	92.4
Cd	91.4	Sb	91.6
Co	90.2	Sn	91.3
Cu	91.0	V	81.7
Mn	72.3	Zn	91.0

Conclusion

The application of impregnated polyurethane foams as sorbents in preconcentration-separation processes is a novel approach in the analytical separations of trace elements from environmental waters. For the purpose of a multielement preconcentration and separation a 1 % solution of DDDC in chloroform was used as advantageous impregnating agent. The sorbed metal chelates were reextracted from the polyurethane foam sorbent by chloroform with 90–93 % recovery. The described preconcentration-separation procedure is utilized in the monitoring of heavy metal pollution of river and drinking waters.

References

1. Braun, T., Navrátil, J. D., and Farag, A. B., *Polyurethane Foam Sorbents in Separation Science*. CRC Press, Boca Raton, 1985.
2. Tóth, J., Palágyi, Š., and Flórián, K., *Abstracts of the 8th Czechoslovak Spectroscopic Conference*, p. 56. Czechoslovak Spectroscopic Society, Prague, 1988.
3. Palágyi, Š., Tóth, J., and Flórián, K., *Proceedings of the XXXIInd Hungarian Spectroscopic Conference*, p. 347. GTE, Budapest, 1989.
4. Braun, T. and Palágyi, Š., *Anal. Chem.* 51, 1697 (1979).
5. Palágyi, Š. and Braun, T., *Analyst* (London) 106, 1326 (1981).
6. Braun, T. and Farag, A. B., *Anal. Chim. Acta* 61, 265 (1972).
7. Starý, J., Kyrš, M., Marhol, M., *et al.*, *Separáční metody v radiochemii*. (Separation Methods in Radiochemistry.) Academia, Prague, 1975.

8. Pradzynski, A. H., Henry, R. E., and Stewart, J. S., *J. Radioanal. Chem.* 32, 219 (1976).
9. Pliešovská, N., *Abstracts of the 26th Colloquium Spectroscopicum Internationale*, Vol. IV, p. 17. University of Sofia, 1989.
10. De, A. N., Khopkar, S. M., and Chalmers, R. A., *Solvent Extraction of Metals*. Van Nostrand Reinhold Co., London, 1970.
11. Koch, O. G. and Koch-Dedic, G. A., *Handbuch der Spurenanalyse*. Springer-Verlag, Berlin, 1974.

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